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(19) (CA) **CANADIAN PATENT** (12)

(54) THERMOPLASTIC MOULDING COMPOUNDS

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THERMOPLASTIC MOULDING COMPOUNDS

Abstract of the Disclosure

Thermoplastic moulding compounds of 1.) 70 - 30 parts by weight of a thermoplastic polycarbonate based on dihydroxy-diarylalkanes, including those which carry chlorine, bromine or methyl groups in the ortho-position to the hydroxyl group and 2.) 30 - 70 parts by weight of a mixture of 25 to 100 % by weight of graft copolymers obtained from monomers polymerised on a rubber and 0 to 75 % by weight of a copolymer of 95 to 50 % by weight styrene, α-methylstyrene, methyl methacrylate or mixtures thereof and 50 to 5 % by weight of acrylonitrile, methacrylonitrile, methyl methacrylate or mixtures thereof, wherein the graft copolymers used are a mixture of a) a graft copolymer of from 50 to 95 % by weight, preferably from 50 to 70 % by weight of a mixture of the monomers styrene and acrylonitrile (in proportions by weight of from 50 : 50 to 95 : 5) or from 5 to 50 % by weight, preferably from 30 to 50 % by weight of a rubber having an average particle size of from 0.1 to 2 µ, preferably from 0.3 to 1 µ, with a degree of grafting of from 0.2 to 0.5, and b) a graft copolymer of from 40 to 10 % by weight, preferably from 35 to 20 % by weight of a mixture of the monomers styrene and acrylonitrile (in proportions by weight of from 50 : 50 to 95 : 5) and 60 to 90 % by weight, preferably 65 to 80 % by weight of a rubber having an average particle size of from 0.1 to 2 µ, preferably from 0.3 to 1 µ, with a degree of grafting of from 0.7 to 0.9, the moulding compound containing the graft copolymers a) and b) in proportions by weight of from 1 : 3 to 3 : 1 and having a rubber content of from 10 to 25 % by weight, preferably from 15 to 20 % by weight.

Mixtures containing from 90 to 30% by weight of a polycarbonate based on aromatic dihydroxy compounds and from 10 to 70% by weight of a graft polymer prepared from polybutadiene and a mixture of acrylonitrile and an aromatic vinyl hydrocarbon have been disclosed in German Auslegeschrift No. 1,170,141. These moulding compounds are distinguished by their good processing quality, but for some technical usages the strength of their coalescence seams is insufficient. Special mixtures of aromatic polycarbonates and ABS polymers in which the strength of the coalescence seam is considerably improved have been disclosed in German Offenlegungsschrift No. 2,259,565.

Since the above moulding compounds lose their impact strength at low temperatures and break with splintering, they are not suitable for use in, for example, motor car manufacturing, in spite of their other satisfactory properties. This is because, in this field, they are required to be either resistant to breakage at $-30^{\circ}C$ or at least to break without splintering at this temperature.

The present invention is based on the finding that the low temperature breakage characteristics of moulding compounds are substantially improved by a combination of two ABS graft copolymers.

The present invention therefore provides a thermoplastic moulding compound having a rubber content of from 10 to 25% by weight which comprises:

(i) 70 to 30 parts by weight of a thermoplastic polycarbonate of bisphenol-A; and

(ii) 30 to 70 parts by weight of a mixture of:

(a) 0 to 75% by weight of a copolymer of 95 to

50% by weight styrene, α-methylstyrene, methyl methacrylate or mixtures thereof and 5 to 50% by weight of acrylonitrile, methacrylonitrile, methyl methacrylate or mixtures thereof; and

(b) 100 to 25% by weight of graft polymers which are a mixture of:

(I) a graft copolymer, having a degree of grafting of from 0.2 to 0.5, of from 50 to 95% by weight of a mixture of the monomers styrene and acrylonitrile in respective proportions by weight of from 50:95 to 95.5 on from 50 to 5% by weight of polybutadiene having an average particle size of from 0.1 to 2μ; and

(II) a graft copolymer, having a degree of grafting of from 0.7 to 0.9, of from 35 to 20% by weight of a mixture of the monomers styrene and acrylonitrile in respective proportions by weight of from 50:50 to 95:5 on from 65 to 80% by weight of polybutadiene having an average particle size of from 0.1 to 2μ, the graft copolymers (I) and (II) being present in proportions by weight of from 1:3 to 3:1.

Preferably, the graft copolymer (I) is a graft copolymer of from 50 to 70% by weight of a mixture of the monomers styrene and acrylonitrile in respective proportions by weight of from 50 : 50 to 95 : 5 on from 50 to 30% by weight of a rubber having an average particle size of from 0.1 to 2μ. It is furthermore preferred that the rubber of each of the graft copolymers (I) and (II) has an average particle size of from 0.3 to 1μ. A further preferred embodiment of the invention is a moulding compound as defined above wherein the rubber content is from

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15 to 20% by weight. The thermoplastic polycarbonate preferably has a molecular weight of from 10,000 to 60,000, particularly from 20,000 to 40,000.

Compared with the known mixtures of aromatic polycarbonates and ABS polymers, the moulding compounds according to the present invention have improved tensile strength and a reduced tendency to splinter at low temperatures. The high strength of the

coalescence seam is unchanged. It was also unexpectedly found that the dimensional stability under heat, determined according to Vicat B, fell only insignificantly with increasing rubber content.

Any thermoplastic polycarbonates preferably from bisphenol A may in principle be used for the moulding compounds according to the present invention. Polycarbonates are known. They are prepared by the reaction of di- or polyhydroxyl compounds with phosgene by known phase interface processes.

They may be prepared by, for example, emulsion polymerisation of the graft monomers with the aid of radical initiators in a rubber latex. The rubber particles in this latex preferably have average diameters of from 0.3 to 1μ . The particles are not substantially increased in size by the graft polymerisation of the monomers, and the

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particles of graft copolymer therefore have the size given above. The terms "particle size" and "particle diameter" are always used herein to denote the average diameter d_{50}, which means that 50% of the particles under consideration are larger and 50% are smaller than the d_{50}. The term "degree of grafting" means the proportion of graft polymerised monomers (i.e. chemically bound to the rubber) to the total quantity of polymerised monomers.

The following rubbers are particularly suitable for use as graft bases:- polybutadiene; butadiene/styrene copolymers containing up to 30% by weight of styrene incorporated by polymerisation; copolymers of butadiene and acrylonitrile containing up to 20% by weight of acrylonitrile; and copolymers of butadiene containing up to 20% by weight of a lower alkyl ester of acrylic or methacrylic acid (e.g. methyl acrylate, ethyl acrylate, methyl methacrylate or ethylmethacrylate).

In addition to the graft polymers, the moulding compound may contain a copolymer of the graft monomers or similar monomers. Copolymers of from 95 to 50% by weight of styrene, α-methylstyrene, methyl methacrylate or mixtures thereof and from 5 to 50% by weight of acrylonitrile, methacrylonitrile, methyl methacrylate or mixtures thereof are suitable. Copolymers of this type are frequently formed as by-products of graft polymerisation, especially when large quantities of monomers are grafted on small quantities of rubber. The properties of the material can therefore be influenced by the addition of such copolymers.

The various constituents of the moulding compounds of the present invention are generally prepared separately and then mixed together in known mixing apparatus such as mixing rollers, double screw extruders or internal mixers. The constituents are generally melted in these mixing processes. In cases where the constituents of the moulding

compound are initially obtained as latices, the latices may, of course, be mixed and then precipitated together. The usual aggregates such as fillers, glass fibres, pigments, stabilizers, flame retarding agents, fluidizing agents, lubricants, mould release agents and antistatic agents may be added in the mixing processes. The moulding compounds of the present invention may be used for the production of all types of moulded articles, and in particular the compounds may be worked up by injection moulding. Their main application lies in cases where good low temperature breakage characteristics are required, e.g. in dashboards, steering column casings, loudspeaker cases and all types of internal parts in motor vehicles. The present invention is further illustrated by the following Examples:

I. Graft polymer with 50 parts by weight of rubber

35 Parts by weight of styrene and 15 parts by weight of acrylonitrile are grafted onto 50 parts by weight of a coarse-particled rubber in which the polybutadiene graft basis (which is in the latex form) has an average particle diameter of from 0.3 to 0.4 μ, using the process of emulsion polymerisation according to German Auslegeschriften Nos. 1,247,665 and 1,269,360.

II. Graft polymer with 80 parts by weight of rubber

14 Parts by weight of styrene and 6 parts by weight of acrylonitrile are grafted onto 80 parts by weight of a coarse-particled rubber in which the butadiene graft basis present in the latex form has an average particle diameter of from 0.3 to 0.4 μ, using the process of emulsion polymerisation according to German Auslegeschriften Nos. 1,247,665 and ~~1,629,360~~ 1,269,360.

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III. Styrene/acrylonitrile copolymer

72 Parts by weight of styrene are polymerised with 28 parts by weight of acrylonitrile by emulsion polymerisation. The copolymer has an intrinsic viscosity of $[\eta]$ = 80.2 (determined in dimethylfuran (DMF) at 20°C).

IV. Aromatic polycarbonate

A polycarbonate based on 4,4'-dihydroxy-diphenyl-propane -2,2 is prepared by the phase interface process. The relative solution viscosity was 1.30 (determined in methylene chloride at 25°C and at a concentration of 5 g/l).

The individual components are mixed in internal kneaders at ca. 260°C and isolated, using a roller followed by band granulating. Various characteristic compounds are shown in the following Table.

The apparatus used in the test for determining the splintering breakage at low temperatures is shown in Fig. 1, in which a molded body (1) formed from the compounds shown in the Table measuring 163 mm in width, 105 mm in depth, 20 mm in height and 3 mm in thickness and cooled to the test temperature, is placed in a support frame (2) inside a refrigeration chamber. A falling hemispherical body (3) 45 mm in diameter and weighing 29 kg is then dropped on the test sample from a height of 2 metres.

The fracture pictures are assessed visually and graded as follows:

0 no damage
1 beginning of a single tear in any position (Fig.2)
2 breakage of body into two (Fig. 3)
3 breakage into two with additional crack (Fig. 4)
4 breakage through the body (Fig. 5)
5 tearing breakage into several fragments still hanging together (Fig. 6)
6 splinter breakage into a large number of parts no longer joined together. (Fig. 7)

TABLE

Product (%)	Example 1	2	3	4	5
I	35.6	12.8	16.0	19.2	25
II	--	20.0	15.0	10.0	5
III	14.4	7.2	9.0	20.8	--
IV	50.0	60.0	60.0	5.0	70
Rubber (%)	17.8	22.4	20.0	17.6	16.5
Low temperature breakage characteristics*					
at -20°C	3.2	0	0	2.0	1.8
at -30°C	5.0	0.8	2.6	1.8	2.6
at -40°C	--	1.6	3.0	1.6	3.0
Vicat B**	117	120	119	116	127

*) average of assessment of breakage pictures from five test samples (Figures 2 - 7)

**) DIN 53 460

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A thermoplastic moulding compound having a rubber content of from 10 to 25% by weight which comprises:

(i) 70 to 30 parts by weight of a thermoplastic polycarbonate of bisphenol-A; and

(ii) 30 to 70 parts by weight of a mixture of:

(a) 0 to 75% by weight of a copolymer of 95 to 50% by weight styrene, α-methylstyrene, methyl methacrylate or mixtures thereof and 5 to 50% by weight of acrylonitrile, methacrylonitrile, methyl methacrylate or mixtures thereof; and

(b) 100 to 25% by weight of graft polymers which are a mixture of:

(I) a graft copolymer, having a degree of grafting of from 0.2 to 0.5, of from 50 to 95% by weight of a mixture of the monomers styrene and acrylonitrile in respective proportions by weight of from 50:95 to 95.5 on from 50 to 5% by weight of polybutadiene having an average particle size of from 0.1 to 2μ; and

(II) a graft copolymer, having a degree of grafting of from 0.7 to 0.9, of from 35 to 20% by weight of a mixture of the monomers styrene and acrylonitrile in respective proportions by weight of from 50:50 to 95:5 on from 65 to 80% by weight of polybutadiene having an average particle size of from 0.1 to 2μ, the graft copolymers (I) and (II) being present in proportions by weight of from 1:3 to 3:1.

2. A thermoplastic moulding compound as claimed in claim 1 wherein the graft copolymer (I) is a graft copolymer of from

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50 to 70% by weight of a mixture of the monomers styrene and acrylonitrile in respective proportions by weight of from 50 : 50 to 95 : 5 on from 50 to 30% by weight of a rubber having an average particle size of from 0.1 to 2 μ.

3. A thermoplastic moulding compound as claimed in claim 1 wherein the rubber of graft copolymer (I) has an average particle size of from 0.3 to 1 μ.

4. A thermoplastic moulding compound as claimed in claim 1, 2 or 3 wherein the rubber of graft copolymer (II) has an average particle size of from 0.3 to 1 μ.

5. A thermoplastic moulding compound as claimed in claim 1, 2 or 3 wherein the rubber content is from 15 to 20% by weight.

6. A thermoplastic moulding compound as claimed in claim 1, 2 or 3 wherein the thermoplastic polycarbonate has a molecular weight of from 10,000 to 60,000.

7. A thermoplastic moulding compound as claimed in claim 1, 2 or 3 wherein the thermoplastic polycarbonate has a molecular weight of from 20,000 to 40,000.

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PATENT AGENTS

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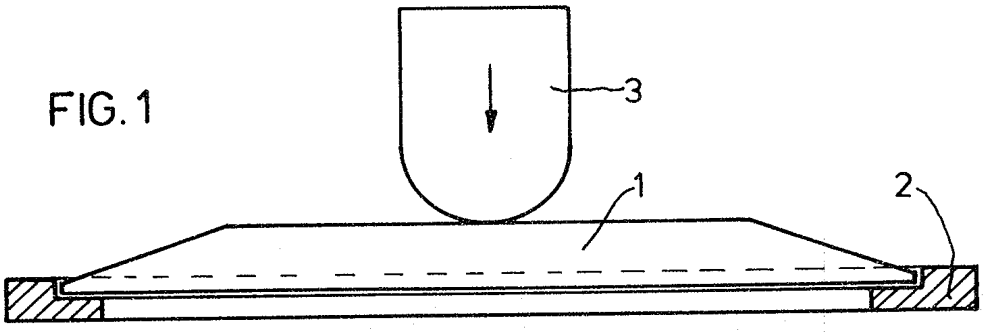
FIG. 1



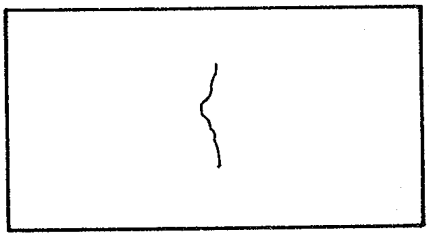


FIG. 2

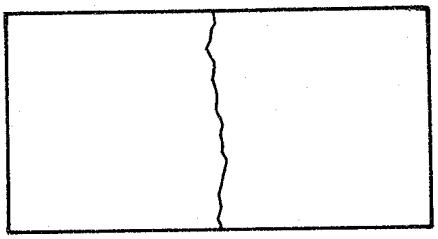


FIG. 3

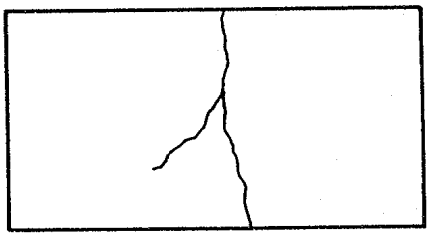


FIG. 4

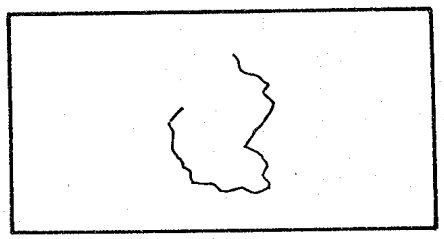


FIG. 5

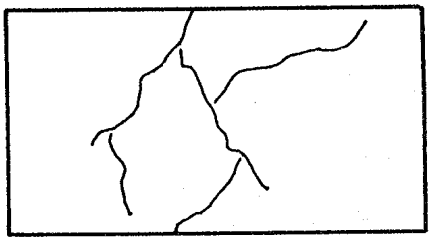


FIG. 6

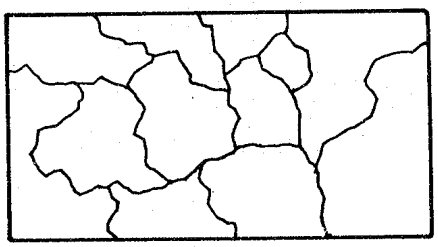


FIG. 7

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